

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

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			0450
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
		01 Sep 2001 - 31 Aug 2003 FINAL	
4. TITLE AND SUBTITLE Modeling of Free Electron Laser Ablation II			5. FUNDING NUMBERS 62227D 0483/01
6. AUTHOR(S) Dr Garrison			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) PENNSYLVANIA STATE UNIVERSITY 110 TECHNOLOGY CENTER BLDG UNIVERSITY PARK PA 16802-7000			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NE 4015 WILSON BLVD SUITE 713 ARLINGTON VA 22203			10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-01-1-0511
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: Unlimited			
20040921 048			
13. ABSTRACT (Maximum 200 words) Development of a coarse-grained chemical reaction model (CGCRM) for incorporation into molecular dynamics (MD) simulations in order to assess the effects of chemical reactions on the ablation process. This model has been successfully applied to the ablation of organic systems and is now being implemented for polymers and biological materials. Development of a combined molecular dynamics and direct simulations Monte Carlo (DSMC) methodology for combining the output from the MD simulations including the presence of clusters into the DSMC calculations that allow for long time and large space development of the plume. Developed a new protocol, substrate-assisted laser-initiated ejection, for mass spectrometry of biological molecules embedded in a water matrix, the simulations were aimed at modeling Charles Lin's (Harvard) drug delivery experiments but have inspired a new set of Mass Spectrometry experiments in Nick Winograd's group (Penn State). Sub-contract to UVa was used to support a graduate (MS.) student, Elodie Leveugle. During the reporting period, the focus of the research project of Ms. Leveugle was on the microscopic mechanisms of photomechanical spallation of molecular targets. It has been revealed in a series of large-scale MD simulations that the relaxation of laser-induced thermoelastic stresses is responsible for the nucleation, growth and coalescence of voids in a broad sub-surface region of the irradiated target. Two stages have been identified in the evolution of voids in laser spallation, the initial void nucleation and growth, with the number of voids of all sizes increasing, followed by void coarsening and coalescence, when the number of large void increases at the expense of quickly decreasing population of small voids.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Air Force Office of Scientific Research

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GRANT NUMBER

F49620-01-1-0511

ANNUAL PROGRESS REPORT
Grant numbers: F49620-01-1-0511

PRINCIPAL INVESTIGATOR: Dr. Barbara J. Garrison

CO-PRINCIPAL INVESTIGATOR: Dr. Leonid V. Zhigilei

INSTITUTION: Penn State University

GRANT TITLE: Modeling of Free Electron Laser Ablation II

REPORTING PERIOD: 1 September 2002 – 31 August 2003

AWARD PERIOD: 1 September 2001 – 31 August 2004

OBJECTIVE: To investigate microscopic mechanisms and dynamics of FEL initiated ablation with a focus on a fundamental understanding of the basic mechanisms of ablation and effects of selective targeting of the laser energy.

APPROACH: We are developing a multiscale computational technology that includes atomistic, mesoscopic/molecular, and continuum levels of description of fundamental processes involved in FEL laser ablation of biological materials.

ACCOMPLISHMENTS: The accomplishments support by this project include as follows:

- Development of a coarse-grained chemical reaction model (CGCRM) for incorporation into molecular dynamics (MD) simulations in order to assess the effects of chemical reactions on the ablation process. This model has been successfully applied to the ablation of organic systems and is now being implemented for polymers and biological materials.
- Development of a combined molecular dynamics and direct simulations Monte Carlo (DSMC) methodology for combining the output from the MD simulations including the presence of clusters into the DSMC calculations that allow for long time and large space development of the plume.
- Developed a new protocol, substrate-assisted laser-initiated ejection, for mass spectrometry of biological molecules embedded in a water matrix. The simulations were aimed at modeling Charles Lin's (Harvard) drug delivery experiments but have inspired a new set of Mass Spectrometry experiments in Nick Winograd's group (Penn State).
- Sub-contract to UVa was used to support a graduate (M.S.) student, Elodie Leveugle. During the reporting period, the focus of the research project of Ms. Leveugle was on the microscopic mechanisms of photomechanical spallation of molecular targets. It has been revealed in a series of large-scale MD simulations that the relaxation of laser-induced thermoelastic stresses is responsible for the nucleation, growth and coalescence of voids in a broad sub-surface region of the irradiated target. Two stages have been identified in the evolution of voids in laser spallation, the initial void nucleation and growth, with the number of voids of all sizes increasing, followed by void coarsening and coalescence, when the number of large void increases at the expense of quickly decreasing population of small voids. The void volume distributions are found to be relatively well described by power law $N(V) \sim V^{-\tau}$, with exponent gradually increasing with time. A similar

volume distribution has been obtained in a series of simulations of uniaxial expansion of the same molecular system performed at a strain rate and temperature realized in the irradiated target. Spatial and time evolution of the laser-induced pressure predicted in the MD simulation has been related to the results of integration of a thermoelastic wave equation and the scope of applicability of the continuum calculations has been discussed.

SIGNIFICANCE: Our simulations give a unique opportunity to study the laser ablation phenomena at molecular level and compose an important part of the effort to better understand the mechanisms of laser damage/desorption/ablation at a microscopic level. The insight provided into these physical processes can help in developing medical applications of FEL.

WORK PLAN: A steady progress in the development of advanced and unique computational methodology and understanding the basic mechanisms of laser interaction with organic materials make a solid foundation for extending the research work to more complex organic systems and addressing complex processes in the expanding ablation plume. Below are some of the directions to be pursued.

- The developed methodology for molecular dynamics modeling of bond breaking/making chemical reactions, such as photofragmentation of excited molecule and the subsequent various chemical reactions, opens up new possibilities in the investigation of photochemical processes. We are developing this methodology for polymer ablation.
- We will continue our analysis of the microscopic mechanisms of laser spallation of organic materials. In the case of spallation, the material disintegration proceeds in the form of void nucleation and growth and is localized within the spallation region at a certain depth under the irradiated surface. Analysis of the laser ablation in this case leads to a more general question on the microscopic mechanisms of the dynamic fracture under conditions of ultra-high strain rate and elevated temperature.

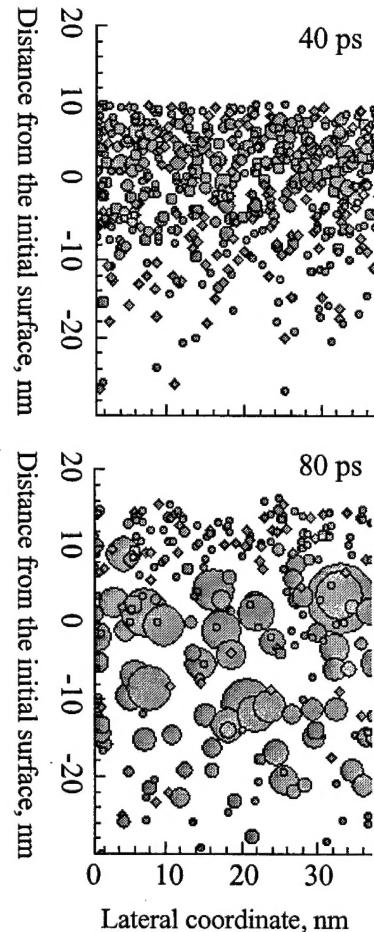


Figure 1. Nucleation and grow of sub-surface voids in a MD simulation of laser spallation. Voids are represented by spheres of the same volume as the actual voids

PERSONNEL SUPPORTED:

Professor Barbara J. Garrison, Principal Investigator, Penn State University

Professor Leonid V. Zhigilei, Co-Principal Investigator, University of Virginia

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Dr. Michael Zeifman, Post Doctoral Researcher, Penn State University

Dr. Uchkun Kutliev, Post Doctoral Researcher, Penn State University

Elodie Leveugle, Graduate (M.S.) Student, University of Virginia

PUBLICATIONS:

- [1] L. V. Zhigilei, Dynamics of the plume formation and parameters of the ejected clusters in short-pulse laser ablation, *Appl. Phys. A* 76, 339-350, 2003.
- [2] L. V. Zhigilei, Y. G. Yingling, T. E. Itina, T. A. Schoolcraft, and B. J. Garrison, Molecular Dynamics Simulations of Matrix Assisted Laser Desorption - Connections to Experiment, *Int. J. Mass Spectrom.* 226, 85-106, 2003.
- [3] B. J. Garrison, A. Delcorte, L. V. Zhigilei, T. E. Itina, K. D. Krantzman, Y. G. Yingling, C. M. McQuaw, E. J. Smiley, and N. Winograd, Big Molecule Ejection - SIMS vs. MALDI, *Appl. Surf. Sci.* 203-204, 69-71, 2003.
- [4] L. V. Zhigilei, E. Leveugle, B. J. Garrison, Y. G. Yingling, and M. I. Zeifman, Computer simulations of laser ablation of molecular substrates, *Chem. Rev.* 103, 321-348, 2003.
- [5] Y. G. Yingling and B.J. Garrison, Photochemical ablation of organic solids, *Nucl. Instrum. Methods B*, 203, 188-194 (2003).
- [6] M. I. Zeifman, B. J. Garrison, and L. V. Zhigilei, A hybrid MD-DSMC model of picosecond laser ablation and desorption, *Rarefied Gas Dynamics: 23rd International Symposium, AIP Conference Proceedings* 663, 939-946, 2003.
- [7] Y. Dou, N. Winograd, B. J. Garrison, and L. V. Zhigilei, Substrate-assisted laser-initiated ejection of proteins embedded in water films, *J. Phys. Chem. B* 107, 2362-2365, 2003.
- [8] B. J. Garrison, T. E. Itina, and L. V. Zhigilei, The limit of overheating and the threshold behavior in laser ablation, *Phys. Rev. E*, 68, 041501, 2003.
- [9] M. I. Zeifman, B. J. Garrison, and L. V. Zhigilei, Evolution of a plume in laser ablation: dependence on the spot size, *Proceedings of the 36th AIAA Thermophysics Conference, AIAA Paper 2003-3493*, 2003.
- [10] E. Leveugle and L. V. Zhigilei, Microscopic mechanisms of short pulse laser spallation of molecular solids *Appl. Phys. A*, submitted, 2003.
- [11] E. Leveugle, D. S. Ivanov, and L. V. Zhigilei, Photomechanical spallation of molecular and metal targets: molecular dynamics study, *Appl. Phys. A*, submitted, 2003 (invited paper for the special issue on femtosecond phenomena).
- [12] Y. G. Yingling, P. F. Conforti, and B.J. Garrison, Theoretical investigation of laser pulse width dependence in thermal confinement regime, *COLA '03 Proceedings, Appl. Phys. A*, submitted.

HONORS AND AWARDS:

- Barbara J. Garrison, Shapiro Professor of Chemistry, 2002-present
- Leonid V. Zhigilei, American Society for Mass Spectrometry, 2002 Research Award Recipient
- Yaroslava Yingling, Best Ph.D. Award from the Materials Research Institute at the Pennsylvania State, April 2003
- Yaroslava Yingling, Braucher Scholarship Award for Graduate Student Research from the Chemistry Department at the Pennsylvania State University, Fall 2002
- Yaroslava Yingling, Gordon Research Conference Travel Award, July 2002
- Elodie Leveugle, "Outstanding Poster Presentation," at the 7th International Conference on Laser Ablation, Crete, Greece, October 2003
- Elodie Leveugle, Travel Grants for Young Researchers through the European Union "Marie Curie Programme, October 2003
- Elodie Leveugle, M.S. Thesis defense, University of Virginia, December 2003